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Optimization of platinum extraction by trioctylphosphine oxide in the presence of alkaline-metal salts

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Abstract

Effect of alkaline metal salts on the solvent extraction of platinum from leached spent dehydrogenation catalysts (Pt/Al_2O_3) in aqua-regia by the Trioctylphosphine oxide (TOPO) has been investigated. Best salting out effect was achieved using KCl as the additive salt in which process upto 90% of Platinum extraction achieved. Response Surface methodology utilized in order to design the experiments, model the extraction process for platinum and aluminum as well as; optimize the whole process. It was shown that solvent extraction of platinum by TOPO was kinetically fast and the needed equilibrium time for it was less than 30 seconds. In the present study, proposed models for platinum and aluminum extractions were reported and optimum conditions determined which led to the highest separation factors.

Keywords: Liquid-liquid extraction; Pt recovery; trioctylphosphine oxide; TOPO; salting-out effect; response surface methodology; RSM; box behnken; design expert; spent catalyst

1. Introduction

Liquid-Liquid Extraction (LLE) also known as solvent extraction is a process of transferring a chemical compound from one liquid phase to another immiscible with the first. For the separation and

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purification of metal ions, this method is known since 1842 [1]. Solvent extraction of platinum from spent petrochemical catalysts reported by different authors in recent years [2-4]. This is important from the viewpoints of economics as well as; environmental protection [5, 6]. In fact, natural resources of platinum are rather limited. On the other hand, the demand for platinum grows considerably each year. Table 1 represents total supply, demand and recycling amounts of platinum from 2005 to 2010 in mega grams.

Table 1. Platinum total supply, demand and recycling (2005 to 2010) [6]

(In Mega grams)	2005	2006	2007	2008	2009	2010
Total supply	206.5	212.4	205.3	184.8	187.4	188.5
Total demand	247.8	245.4	257.3	248.5	211.3	245.1
Total recycling	-39.5	-44.0	-49.5	-56.9	-43.7	-57.2

All solvent extraction processes are based upon the chloro complexes of the platinum, as chloride is the only effective medium by which the platinum can be brought into solution [7]. It has been shown that chloro-complex of platinum could be selectively extracted by amines and neutral extractants[8]. Tertiary amines or solvating extractants are more suitable at high concentration of HCl[5]. In the present study, trioctylphosphine oxide (TOPO) has been used to extract platinum from leach liquors of spent catalysts in aqua-regia. To date, the most important application of TOPO have been in the recovery of uranium from wet process phosphoric acid [9]; However Dhadke et al. [10] reported that TOPO which is a neutral extractant is superior reagent for extraction of platinum in their published short communication. In our experiments, we used alkaline metal salts as additives for enhancement of percentage of platinum extraction. Similar procedure were conducted by Jin-young Lee et al.[1] using various salts alongside the main extractant which was bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) for extraction of platinum (IV) from acidic solutions. In general, aquous solutions containing non-volatile electrolytes such as salts, are of increasing importance in chemical separation processes. The electrolyte influence must be considered both in the process design and operation, because it can affect the thermodynamic equilibrium of the system [11]. The presence of this dissolved salt changes significantly the phase equilibrium behavior of a mixture. This phenomenon is often referred to as salting-in or salting-out effect. It can be used to optimize separation processes [12]. In this study, we tried to find the best salting-out effect of alkaline metal salts and to optimize the solvent extraction of platinum in the presence of such an effect. The salts known as liquid ion exchangers, such as alkylammonium chlorides and alkylphosphonium chlorides, can also be used for the extraction of Pd and Pt [13]. TOPO, diluted in toluene, in presence of alkaline metal salts included NaCl, KCl and LiCl showed huge potential to extract platinum from aqua-regia in the presence of base metals specially aluminum. In this report, optimum conditions to separate the two metals were calculated.

Nomenclature

A	extractant concentration
B	KCl concentration
C	contact time
D	distribution coefficient
K'_{ex}	apparent extraction equilibrium constant

R	TOPO
SF	separation factor

2. Experimental

2.1. Apparatus and reagents

Inductively coupled plasma optical emission spectrophotometer (ICP-OES) was used to analyze platinum and aluminum amounts in the aquous phase before and after the extraction process. Amounts in organic phase were calculated with simple mass balance. TOPO as well as; LiCl and NaCl salts were supplied by the Merck Chemicals hence used without further purifications. Spent catalysts were sample of Pt/Al_2O_3 dehydrogenation catalysts used in petrochemical processes and supplied by the Iran's Petrochemical Research and Technology Company.

2.2. Leaching process chemistry

In the present study, aqua-regia (HCl 3:1 HNO3) was used in order to leach spent catalysts by heating up to 100˚C for about 1h. Table 2 represented the result of leaching aqua-regia.

Table 2. Concentration analysis of the aqua-regia used for leaching spent catalysts

Species	amount in aqua regia (mg/l)
Platinum	34.90
Aluminum	182.50

From the literature studies[14], it might be concluded that platinum contained in the spent catalysts are leached out from the catalyst matrix by concentrated Hydrochloric acid and Nitric acid as the sole oxidizing agents in the form of Chloro-complex $[PtCl6]^{-2}$. Platinum is converted according to the following stoichiometry [15]:

$$8H^{+} + 8\,Cl^{-} + 2NO_3^{-} + Pt \rightarrow [PtCl6]^{-2} + 4\,H_2O + 2NOCl \quad (1)$$

2.3. Liquid-liquid extraction procedure

Equal volumes of aquous phase and organic phase rich of TOPO (20 ml) were equilibrated for various contact times according to designed experiments. After that period, the aquous phase was separated and its metal concentrations were analyzed by ICP-OES. Organic phase loading amounts were calculated by simple mass balance. All the extraction experiments were carried out at ambient temperature.

2.4. Platinum extraction chemistry by TOPO

Platinum (IV) extraction chemistry has been reported in the open literature. Mhaske *et al.* suggested that the extraction of platinum (IV) from the chloride media with TOPO proceeds through ion-pair mechanism as follows (where R is TOPO) [16]:

$$[PtCl6]^{-2} + 2\,H^{+} + 4R \rightarrow (H^{+}.2R)_2\,[PtCl6]^{-2} \qquad (2)$$

If $(H^{+}.2R)_2$ [PtCl6] $^{-2}$ was assumed to be the only species formed in the organic phase, the relation between the distribution coefficient (D) and the apparent extraction equilibrium constant (K'ex) would have been given as[16]:

$$\log D = \log K'ex + 2 \log [H^{+}] + 4 \log [R] \qquad (3)$$

2.5. Response Surface Methodology (RSM) technique

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. The main idea of RSM is to use a set of designed experiments to obtain an optimal response. RSM tries to simplify the original problem through some polynomial estimation over small sections of the feasible area, elaborating on optimum provision through a well known optimization technique, say Gradient Method[17]. In this study, Design Experts software (Version 8.0.1) was employed for the design of experiments, mathematical modelling and optimisation. To obtain rational results by RSM, three steps ought to be considered. The first step in a successful RSM optimisation is to design the experiments for evaluating the model parameters efficiently. The second step is to develop a polynomial model fitted to the experimental data through regression and then to check the model's suitability by applying a statistical test (e.g., Lack-of-fit, F-test) [18-20]. The third or finally is to determine the value of factors satisfying the optimum conditions. Usually, a first or second order polynomial is used for the RSM analysis; furthermore, for responses which include a curvature, a second order polynomial is preferred. The general form of such polynomial is as follows:

$$y = a_0 + \sum_{i=1}^{k} a_i x_i + \sum_{i=1}^{k} a_{ii} x_{ii}^{2} + \sum_{i}^{k}\sum_{j}^{k} a_{ij}\, x_i x_j \quad (i < j) + \varepsilon \qquad (4)$$

where, y is the predicted response, a_0 is a constant, a_i is the ith linear coefficient, a_{ii} is the ith quadratic coefficient, a_{ij} is the ith interaction coefficient, x_i is the independent variable, k is number of factors and ε is the associated error. In addition, the coefficients of the model are predicted through regression. Details of the parameter estimations for such a model are reported elsewhere[18,20]. It was assumed that

the most important variables on the Pt extraction could be extractant concentration, contact time and additive concentration. The proposed levels of these variables are demonstrated in Table 3:

Table 3. Experiments designed by RSM (Box-Behnken method) for 3 numeric factor varied over 3 levels with 5 center points per block resulting in 17 runs

Name of variable	Unit	Low	High
Contact time	seconds	30	1800
Extractant concentration	mmole/lit	20	150
KCl concentration	mole/lit	0.00	1.00

Response surface methodology, Box-Behnken, was used to design the experiments by the "Design Expert" software. Extraction percentages of Al and Pt and their distribution ratio are calculated according to the following equations and listed in Table 4. The distribution and separation factors (SF) of the metal between the two phases may be expressed by the following equations [1,21]:

$$Distribution\ Factor = \frac{[Complex]_{(org)}}{M^{m+}_{(aq)}} \quad (5)$$

$$Separation\ Factor = \frac{D_{Pt}}{D_{Al}} \quad (6)$$

Table 4. ICP analysis results for 17 experiments

Extractant conc. (mmole/lit)	Contact time (seconds)	KCl conc. (mole/lit)	Pt extraction (%)	Al extraction (%)	Sep. Factor
85	30	0.0	30.74	10.33	4.00
85	915	0.5	61.89	42.8	2.22
85	915	0.5	64.46	41.42	2.54
85	*30*	*1.0*	*73.06*	*19.34*	*11.78*
85	915	0.5	71.06	41.97	3.40
150	1800	0.5	84.24	38.79	8.48
20	915	1.0	90.26	45.09	11.29
20	30	0.5	80.51	39.01	6.45
20	915	0.0	23.21	38.57	0.48
20	1800	0.5	57.31	42.74	1.79
150	915	1.0	83.23	33.06	10.14
85	1800	0.0	8.13	24.00	0.28
85	915	0.5	69.97	26.86	6.30
150	915	0.0	0.00	25.55	0.00
85	915	0.5	73.86	32.38	5.90
85	1800	1.0	87.30	31.18	15.28
150	30	0.5	66.73	30.04	4.67

3. Results and discussion

3.1. Effect of alkaline metal salts

NaCl, LiCl and KCl were used as the additives in the contact period in the process in which all other parameters including temperature, contact time and extractant concentrations remained constant. Table 5

represented results of experiments utilizing different salts. As it might be inferred, the best extraction percentage as well as; the highest separation factor for platinum over aluminum achieved using KCl as the additive salt. In general, addition of alkaline metal salts displayed impressive effects on improvement of platinum extraction by TOPO in toluene. The enhancement in percent extraction in the presence of added salts might have been due to a common ion effect as well as; the presence of mixed metal salt species making the metal more favourable for extraction [22].

Table 5. Effect of alkaline metal salts on the extraction of Pt and Al (Salt Concentration 1mol/lit, Contact Time 30 Sec. and Extractant Concentration 85 mmole/lit)

Salt type	Pt extraction (%)	Al extraction (%)
NaCl	30.37	42.41
LiCl	45.53	48.86
KCl	73.06	19.34

3.2. Pt extraction proposed model

By the help of the "Design Expert" software, it was determined that the most important factors in Pt extraction are B, B^2, AC consequently, the relationship obtained as follows:

$$\text{Pt Extraction} = 70 + 33.97B + 10.18AC - 20.51B^2 \quad (7)$$

Where, A stood for extractant concentration while B and C declared KCl concentration and contact time, respectively. This meant that the contact time or extractant concentration was not as important as the KCl concentration however; these two factors displayed co-interactions. The power of the B showed that the extraction to B had extremism. The negative coefficient showed that there was a maximum here. The following figures illustrated changes of Pt extraction due to proposed variables (Fig. 1 and Fig. 2).

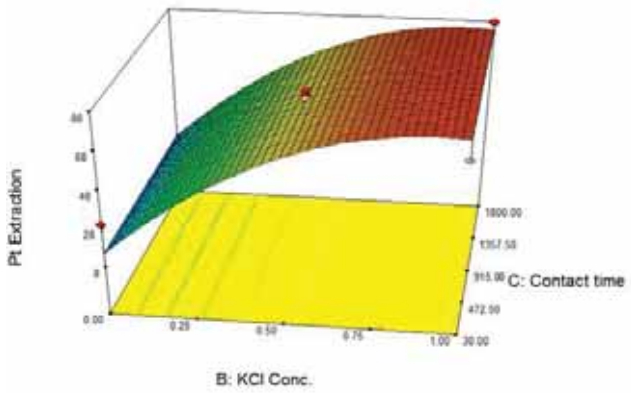

Fig. 1. Pt extraction change due to KCl concentration and contact time, Extractant Concentration 85.00 mmole/lit

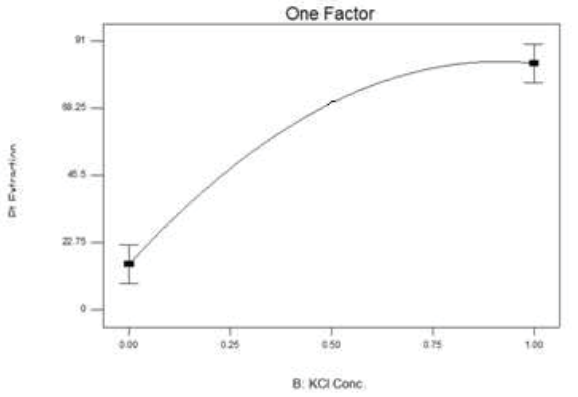

Fig. 2. One-dimensional Pt extraction (%) as a function of KCl concentration mole/lit in the presence of extractant concentration of 85.00 mmole/lit and Contact Time of 915 Seconds

3.3. Aluminum extraction proposed model

According to considerable importance of Aluminum co-extraction with Platinum, here the process of Al extraction by TOPO is reviewed. As in the previous case, a model was obtained based upon important variables as follows:

$$\text{Al Extraction} = 36.94 - 4.75A + 3.78B + 4.75C + 7.53A^2 - 8.90B^2 - 6.83C^2 \quad (8)$$

The 3-D behavior of Al extraction displayed in Fig. 3. It was revealed that at red points, a minimum Al extraction location existed which led to an optimum point where the separation factor was maximum.

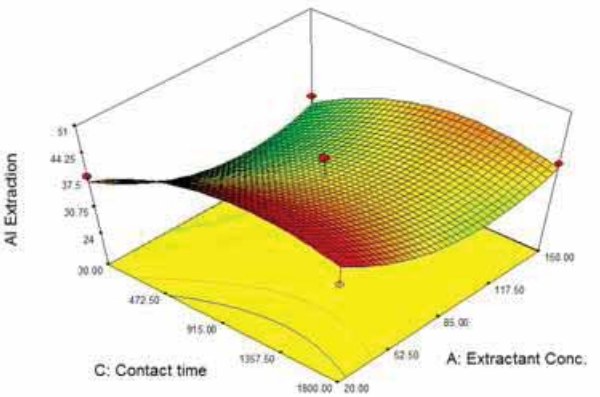

Fig. 3. Al extraction (%) to contact time (s) and extractant concentration (mmole/lit) in the presence of KCl concentration of 0.5 mole/lit.

3.4. Analysis of Variance (ANOVA)

The ANOVA results displayed in Tables 6-7 confirmed that these models might be applied to the considered design space. The F-value for Equations (7) and (8) were 52.76 and 8.42, respectively. From Equation (7), there was only a 0.01% chance that a "Model F-Value" having the same great magnitude could occur due to noise. A very low probability value for model proposed Equation (7) (p-value<0.0001) implied that they were significant for the 95% confidence interval (i.e., p-value less than 0.05 indicate significance). The comparison between residual error and pure error was made through the "lack of fit test". As may be seen from tables 6-7 for both responses, the p-value for the lack of fit test was greater than 0.05; thus, as for the former, the latter was insignificant. The adjusted and predicted values are nearly the same that confirmed the proposed models are satisfactory. Also be noted, the precision of Equation (8) is lower than Equation (7) because of R-Square values.

Table 6. Analysis of Variance (ANOVA) for aluminum extraction (Adj-R^2= 0.7355, Pre-R^2= 0.6624)

Source	Sum of Square	DF	Mean Square	F Value	P Value Probability > F
Model	1220.81	6	203.47	8.42	0.0019
Residual	241.77	10	24.18		
Lack of Fit	47.58	6	7.93	0.16	0.9740
Pure Error	194.19	4	48.55		
Correlation total	1462.58	16			

Table 7. Analysis of Variance (ANOVA) for platinum extraction (Adj-R^2= 0.9066 and Pre-R^2= 0.8659)

Source	Sum of Square	DF	Mean Square	F Value	P Value Probability > F
Model	11428.67	3	3809.56	52.76	< 0.0001
Residual	938.59	13	72.20		
Lack of Fit	841.45	9	93.49	3.85	0.1035
Pure Error	97.14	4	24.29		
Correlation total	12367.27	16			

3.5. Thermodynamic and Kinetic observations

In order to achieve the optimum contact time for quantitative extraction of platinum complex $[PtCl6]^{-2}$, we plotted the Pt extraction percentage over the contact time. It can be inferred from the Fig. 4 that the Pt extraction has a very slight increase by time after the first half a minute. It means that most of the Pt was extracted in the first 30 seconds. After the first 30 seconds, the influence of time is not of any importance. Therefore the equilibrium time is less than 30 seconds and the Pt extraction by TOPO is kinetically fast. This fact may resolve the problem of time-consuming extraction of Platinum by different extractants such as Cyanex 302[1] in which the equilibrium time reported to be 1800 seconds (30 min);

However a similar fast process observation and 1 min equilibrium time was previously reported by Dhadke et al. [10].

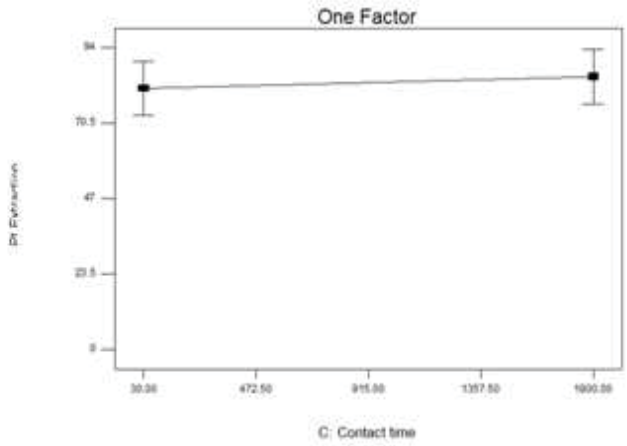

Fig. 4. One-dimensional Pt extraction (%) as a function of contact time (seconds) in the presence of Extractant Concentration 107.84 mmole/lit and KCl Concentration 0.96 mole/lit

3.6. Optimization of platinum extraction

Finding the optimum points were conducted by the help of the numerical optimization part of the Design Expert analysis software. 23 points were calculated and one of them was suggested by the software (Table 8). This was the best operating point where the separation factor was nearly maximum (11.05).

Table 8. Optimized operating points

Extractant conc. (mmol/lit)	KCl conc. (mol/lit)	Contact time(sec.)	Pt extraction (%)	Al extraction (%)	Separation Factor	Desirability
58.39	1.00	30.04	90.2606	23.4469	11.0545	0.827
57.95	1.00	42.62	90.2599	23.7821	11.0545	0.826
58.66	1.00	30.00	90.2597	23.5009	11.0156	0.825
64.87	1.00	30.01	89.0341	22.4339	11.0545	0.825
67.30	1.00	30.00	88.5731	22.0921	11.0545	0.824
59.11	0.99	30.00	90.2570	23.6013	10.9461	0.823
60.56	1.00	96.55	89.4304	24.4357	11.0545	0.820
39.64	1.00	30.00	93.8140	27.2211	11.0545	0.813
47.59	1.00	267.97	90.2600	29.9221	11.0545	0.800
134.35	1.00	1799.99	87.8102	30.4754	11.0545	0.788
133.77	1.00	1800.00	87.7380	30.4159	11.0545	0.788
137.01	1.00	1799.08	88.1323	30.7705	11.0544	0.788
127.04	1.00	1799.99	86.9055	29.8184	11.0545	0.787
126.01	1.00	1799.99	86.7785	29.7414	11.0545	0.787
121.00	1.00	1800.00	86.1653	29.4338	11.0488	0.786
117.77	1.00	1799.99	85.7591	29.2598	11.0545	0.785
138.49	1.00	1766.28	88.0705	31.2613	11.0545	0.785
113.36	1.00	1799.99	85.2139	29.1014	11.0545	0.784
120.51	1.00	1484.14	84.7409	31.7010	11.0545	0.769
109.97	1.00	1355.60	83.7133	31.7761	11.0545	0.764
110.77	1.00	850.98	82.4507	30.7385	11.0545	0.764
105.59	1.00	938.19	82.8243	31.1878	11.0545	0.764
103.53	1.00	1027.97	82.9996	31.5699	11.0545	0.763

4. Conclusion

Solvent extraction developed by salting-out effect of alkaline metal salts was performed to extract platinum from leached spent petrochemical catalysts and separate platinum from aluminum support. Experimental results indicated that that the KCl had the best salting-out effect to reach a quantitative extraction of platinum from leached liquors in comparison with the NaCl and LiCl. Upto 90% of platinum extracted using TOPO by addition of KCl. Equilibrium time, to extract platinum quantitatively, calculated to be less than 30 seconds provided a very kinetically fast approach to extract platinum from aqua-regia. In addition, loading capacity of the metal was quite good and the phase separation was fast. The method was proven to be suitable for recovery of platinum from spent petrochemical catalysts as it did not require the use of different extractants, re-extraction steps or the use of ion exchange columns.

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